# RESEARCH PLAN PROPOSAL

**on the title**

## " DIELECTRIC RELAXATION STUDIES OF SOME PHARMACEUTICALLY IMPORTANT POLAR AROMATIC COMPOUNDS AT MICROWAVE FREQUENCIES"

Submitted for registration to the degree of

**Doctor of Philosophy**

**IN THE FACULTY OF SCIENCE**

## THE IISUNIVERSITY, JAIPUR


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**December, 2014**

## Introduction :

A **dielectric material** (**dielectric** for short) is an electrical insulator that can be polarized by an applied electric field. When a dielectric is placed in an electric field, electric charges do not flow through the material as they do in a conductor, but only slightly shift from their average equilibrium positions causing dielectric polarization. Because of dielectric polarization, positive charges are displaced in the direction of the field and negative charges shift in the opposite direction. This creates an internal electric field that reduces the overall field within the dielectric. If a dielectric is composed of weakly bonded molecules, the molecules not only become polarized, but also reorient so that their symmetry axis aligns with the electric field. (Encyclopedia 2009)

The study of dielectric properties reveals the storage and dissipation characteristics of the material interacting with the electric and magnetic field, and hence its suitability for various applications can be determined. Dielectrics are important for explaining various phenomena in electronics, optics and solid-state physics.

A **liquid dielectric** is a dielectric material in liquid state. Its main purpose is to prevent or rapidly quench electric discharges (Murphy et al., 2013) Dielectric liquids are used as electrical insulators in high voltage applications, e.g. transformers, capacitors, high voltage cables and switchgear. A good liquid dielectric should have high dielectric strength, high thermal stability and chemical inertness against the construction materials used in the devices, low toxicity, good heat transfer properties and low cost. Some examples of dielectric liquids are transformer oil, perfluoroalkanes and purified water.

The momentary delay (or lag) in the dielectric polarization of a material with respect to the varying electric field is called **Dielectric relaxation**, which is caused due to molecular inertia and inability of the dipoles to follow the changing electric field. This occurs both in solid and liquid dielectric like inside capacitor or a solid dielectric placed between two large conducting surfaces connected to an alternating electric source. Relaxation in general is a delay or lag in the

response of a linear system and therefore dielectric relaxation is measured relative to the expected linear steady (equilibrium) state of the dielectric.

**Dielectric relaxation** at microwave frequencies, in addition to molecular relaxation, also includes t\e distortions related to ionic and electronic polarization. The character of the distortion process depends on the structure, composition and surroundings of the sample, as well as the frequency of the electromagnetic radiation.

The dielectric constant of a substance is defined as the ratio of its electrical permittivity to the permittivity of the free space. It is the measure of the extent to which a material concentrates electric flux, and is the electrical equivalent of relative magnetic permeability.

As the dielectric constant increases, the electric flux density in the material increases provided if all other factors remain unchanged. This enables an object of given size, such as a set of metal plates, to hold electric charge for long periods of time. Materials with high dielectric constant are useful in the manufacturing of high-value capacitors.

Dielectric constant is a molecular property of substances, which arises due to contribution from orientational, vibrational and electronic polarization of the molecules and/or atoms. Dielectric spectroscopy investigation mainly probes the effect of weak forces and helps to understand intermolecular reorientational dynamics of the solute and solvent molecules.

Most of the dielectric relaxation processes reported in the literature are aimed at understanding the behavior of dilute solutions of polar substances in non-polar liquids. Though the non-polar liquid does not itself undergo relaxation but it alters the relaxation time of the solute molecule by reducing the internal field and changing the viscosity.

The dielectric studies of binary mixtures of polar molecules are important for understanding the intermolecular interactions in the mixture arising due to the dipole-dipole interaction, hydrogen bonding etc. (Vyas et al., 2011) Dielectric characterization has great potential in studying the phenomenon like, H-bond interactions, dipolar alignment, hydrogen bond connectivity etc.

## Review of Literature :

The studies of dielectric properties of polar liquids, especially in dilute solutions with non-polar medium have important role in liquid state. Gedam et al., (2013) concluded that the dielectric investigations mainly probe weak forces between the molecules and help to understand intermolecular reorientation dynamics of the solute. The values of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) of polar liquids in dilute solution of benzene increase as a function of concentration of polar substance. Sahoo et al., (2012) observed that the simple Debye model of polar and non polar liquids can satisfactory explain the dielectric behavior of amides and acetone under static and high frequency electric fields.

In the study of dielectric behavior of polar and non-polar molecules and their mixtures under varying conditions of composition and temperature, it was found by Kamble et al.,( 2011) that excess properties, which depend on the composition and/or temperature, are of great importance for the characterization of the interaction between components. Refractive index and density measurements of solvent mixtures are expected to shed some light on the solvent-solvent interaction and configuration of their mixtures. These properties have been used to study the structure and solvent-solvent interaction of binary mixtures. Solvent structure determines the nature of interactions between the like and unlike molecules of a liquid binary mixture.

Gedam et al., (2013) carried out measurement of dielectric constant ($\varepsilon'$) and loss factor ($\varepsilon''$) for a polar liquid benzonitrile in a non-polar medium (benzene) at a single microwave frequency (10.15GHz.) at room temperature. They calculated the dielectric parameters by using Smyth's method., Gopala Krishna single frequency concentration method based on Debye equation to analyze the dielectric data ($\varepsilon'$ and $\varepsilon''$) to obtain relaxation time ($\tau$) and electric dipole moment ($\mu$) to explore the molecular structure .The results are discussed to interpret the molecular structure in terms of relaxation time ($\tau$) and electric dipole moment ($\mu$) of reorientation motion of the dipole in the medium.

The molecular interactions between the polar systems of *p*-hydroxy dodecyl benzoate (12HB) and isoproponal for various volume fractions were studied by Shastry et al., (2014) at room temperature to determine the frequency dependent complex dielectric permittivity, by using Abbe's refrectometer at optical frequencies ($10^{15}$Hz) by cavity perturbation technique at the microwave frequencies in X-Band at 10 GHz and LCR meter at 1KHz. The relaxation times and dipole moments for the binary mixtures were calculated using Higasi's method. The above studies indicated the formation of hydrogen bond in the mixtures. There is an increase in the dipole moment as the concentration of benzoate is increased in solute system in non-polar solvent (benzene) and it was obtained to the formation of hydrogen bond between the solute systems. The confirmation of hydrogen bond is confirmed through theoretical studies. The conformational analysis of the formation of hydrogen bond between dodecyl hydroxyl benzoate and isopropyl alcohol is supported by the experimental FTIR spectral studies and theoretical computational methods.

Kumar et al., (2011) calculated the dielectric relaxation and dipole moment of binary mixtures of ethylene glycol, propylene glycol and butylene glycol with dilute solutions of 1, 4-Dioxane for different concentration at 33°C. The static dielectric constants ($\varepsilon'$) of glycols, like ethylene glycol, propylene glycol and butylene glycol in dilute solutions of 1,4-Dioxane were determined at 303K. The measuring frequency of the dipole meter was 2MHz. X-band and J-band microwave benches operating at 9.52GHz and 7.72GHz were used for determination dielectric permittivity ($\varepsilon'$) and dielectric loss factor ($\varepsilon''$). The values of molecular relaxation time ($\tau_0$) and dipole moment ($\mu$) for different compositions of binary mixtures were determined using Higasi's method. They concluded that the relaxation time values increase with increasing viscosity of the medium.

The relaxation time ($\tau$) of three pure compounds methylene dichloride, methyl acetate and 2-methoxy ethanol in a non-polar solvent benzene at microwave frequency of 21.4 GHz at 300K using different concentrations have been calculated by Rajan et al., (2014). The relaxation times were determine by them using Higasi's method and dipole moment was calculated by employing both the Higasi's method and Guggenheim's method. Different dielectric parameters like dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) at microwave frequency (21.4 GHz), static

dielectric constant ($\varepsilon_0$) and optical dielectric constant ($\varepsilon_\infty$) are determined by them for the above mentioned compounds. Using these parameters, various relaxation times viz., average relaxation time ($\tau_0$), molecular relaxation time ($\tau_1$) and group relaxation time ($\tau_2$) of individual components were calculated by them using Gopalakrishna method. It was observed that the relaxation time is very closely related with molecular parameters, such as size, shape and nature of the solute molecules.

The variation of dielectric parameters of the binary mixtures of benzamide and 1-propanol in dilute solutions with benzene was studied by Jain et al., (2012) at four different temperatures. The investigations were made for three different mole fractions of benzamidein 1-propanol at a microwave frequency of 9.385 GHz. The values of dielectric constant ($\varepsilon'$) and dielectric loss factor ($\varepsilon''$) were calculated by using the method given by Heston et al(1950). Permittivity at optical frequencies ($\varepsilon_\infty$) and in the low frequency limit ($\varepsilon_0$) were measured by them with the help of Abbe's refractometer and dipolemeter respectively. The values of relaxation times for molecular and intramolecular rotations were calculated by using Higasi's method. It was observed from the calculations that the values of various relaxation times $\tau_1$, $\tau_2$ and $\tau_0$ for binary mixtures decrease systematically with increase in temperature.

Sastry et al., (2012) investigated the molecular interactions between the polar systems propan-1-ol with alkyl benzoates (methyl benzoate and ethyl benzoate) for various mole fractions at different temperatures by determining the dielectric permittivity using - LF impedance analyzer, microwave bench and Abbe's refractometer in radio, microwave and optic frequency regions respectively. The excess dielectric and thermodynamical parameters - dipole moment, excess dipole moment, excess Helmholtz free energy, excess permittivity, relaxation time, excess inverse relaxation and excess thermodynamic values were computed for the pure and binary mixtures of system 1(1PN + Methyl Benzoate) and system 2 (1PN + Ethyl Benzoate).The formation of Hydrogen bonding between the mixture components was identified by studying the variations in the parameters listed above. The values of dipole moment and excess dipole moment were also determined theoretically using quantum mechanical calculations and were found to be in good agreement with the experimental values.

Narwade et al., (2011) calculated the values of dielectric constant ($\varepsilon'$) and dielectric loss($\varepsilon''$) for n-propylalcohol, ethylenediamine and their binary mixtures in 1,4-dioxane at different temperatures using X-band microwave bench. The relaxation time ($\tau$) and dipole moment ($\mu$) were calculated by employing Gopala Krishna's method. Values of relaxation time ($\tau$) were compared with the calculated values obtained by using different methods. The thermodynamic parameters were also calculated for dielectric relaxation as well as for viscous flow process. Observed values of Debye's factor and Kalman's factor show that Kalman's formula satisfactorily explains the relationship between dielectric relaxation time and the viscosity. The non-linear behavior of relaxation time with mole fraction reveals the presence of solute-solute molecular association in the mixture. These studies suggest the dipole-dipole molecular association in the mixture through hydrogen bonding.

Sharma et al., (2007) calculated the dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) for dilute solutions of ethanol in benzene at 9.883 GHz at 25, 30, 35 and $40^0$C using standard microwave techniques. The dielectric relaxation time ($\tau$) and dipole moment ($\mu$) at these temperatures were calculated by using the single frequency concentration variation method suggested by Gopala Krishna. It was found that the dielectric relaxation process can be treated as a rate process like the viscous flow process. Based upon these studies, the presence of solute-solvent associations has been proposed. The energy parameters for the dielectric relaxation process were calculated by them and compared with the corresponding energy parameters of viscous flow process.

Ganesh et al., (2014) investigated the dielectric properties of the binary mixtures of 1-propanol and phenol at a constant temperature of 303K in dilute solutions of benzene using standard standing technique at microwave X-band (9.4 GHz) and J-band(7.4 GHz) frequencies. The values of different dielectric parameters $\varepsilon_{0,}$ $\varepsilon_{\infty,}$ $\varepsilon'$ and $\varepsilon''$ were determined by them for five different mole fractions of 1-propanol and phenol. The values of permittivity and dielectric loss were used to evaluate relaxation time for overall molecular rotation ($\tau_1$), relaxation time for intermolecular rotations ($\tau_2$), most probable relaxation time ($\tau_0$) and dipole moment ($\mu$) at the constant temperature 303K. The values of relaxation times and dipole moment were found to increase as the mole fraction of 1-propanol, in binary mixtures increases. These investigations

suggest the existence of both the intermolecular and intramolecular orientations taking place in both the binary mixtures.

Ganesh et al., (2014) calculated the dielectric relaxation time (τ) and dipole moment (μ) for different molar concentrations of acetone in binary mixture of acetone and ethylmethyl ketone at two microwave frequencies, viz; 9.88 GHz and 7.42 GHz, in dilute solution of carbon tetrachloride at constant temperature (303K). The dielectric constant ($\varepsilon'$) and dielectric loss factor ($\varepsilon''$), static permittivity ($\varepsilon_0$) and dielectric constant at optical frequencies ($\varepsilon_\infty$) were determined. The relaxation time (τ), dipole moment (μ) and energy of activation parameter were also determined. The values of relaxation times were not found to decrease with increase of molar fraction of acetone in the binary mixture of acetone and ethylmethyl ketone. While the dipole moment decreases with the increase in both the systems, excess volume of binary mixtured solution is found to be negative for all the systems.

Khan et al., (2010) found the dielectric absorption behavior of H-bonded complexes of methyl methacrylate (MMA) and butyl methacrylate (BMA) with *p*-cresol, *p*-chlorophenol, 2,4-dichlorophenol and *p*-bromophenol at a microwave frequency of 9.37 GHz in dilute solution of carbon tetrachloride at 308K. Different dielectric parameters like dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) at microwave frequency (9.37 GHz) were determined by them along with the static dielectric constant ($\varepsilon_0$) and dielectric constant at optical frequencies ($\varepsilon_\infty$). The multiple relaxation time ($\tau_1$) was found to be a function of the hydrogen bonding strength of phenolic hydrogen, whereas the group rotation relaxation time ($\tau_2$) varies as a function of the static interaction of proton donor and the relaxation time is maximum at 50:50 mol% ratio.

Jain et al., (2013) studied the dielectric relaxation behavior of the binary mixture of nicotinamide and 1-butanol at four different temperatures viz. 303K, 313K, 323K and 333K in dilute solutions of benzene at a constant frequency of 9.385 GHz. The values of different dielectric parameters namely $\varepsilon_0$ (static permittivity), $\varepsilon'$ (dielectric constant), $\varepsilon''$ (dielectric loss factor) and $\varepsilon_\infty$ (optical permittivity) were determined by using standard methods. The measured values of permittivity and dielectric loss were used to evaluate the relaxation time (τ) and the dipole moment (μ) by Higasi method at different temperatures. The energy parameters for dielectric relaxation process

of the mixture were calculated at various temperatures and comparison was made with the corresponding energy parameters for viscous flow process. It was found that the dielectric relaxation process can be treated as the rate process, just like the viscous flow process. This study suggests the existence of both the intermolecular and overall molecular rotation in the binary mixture.

Maharolkar et al.,( 2012) investigated the density (ρ), refractive index ($n^D$), dielectric constant ($\varepsilon'$) and relaxation time (τ) of binary mixture of Allyl Bromide (AB) with polar protic solvent 2-Butanol including those of the pure liquids over the complete composition range. The experimental data is used to calculate excess molar volumes ($V^E_m$), excess dielectric constant ($\varepsilon^s_E$), excess inverse relaxation time (1/τ)E, excess molar refraction (Rm)E, the Bruggeman factor .The values of refractive index and density were found to increase with increase in volume fraction of AB. The value of $\varepsilon^s_E$ decreases as the concentration of AB increases.

## Methods to determine dielectric properties:

Several techniques are used to measure the dielectric properties of the materials. Icier and Baysal (2004) have listed different measurement techniques. In general, the choice of measuring equipment depends on the material, the required frequency range, accuracy desired and both availability and cost of equipments (Nelson and Kraszewski, 1990)

The three most popular methods for measuring dielectric properties of materials are:

1) The open-ended coaxial probe method.

2) The transmission line method.

3) The resonant cavity method.

The open-ended coaxial probe method using the network analyzer has been the preferred method for measuring dielectric properties as it can measure dielectric properties over a wide frequency range. It is easy to use and it can be used for liquids and solids equally well (Engelder and Buffler, 1991). The second method used to measure dielectric properties of

materials is the transmission line method using the waveguides, which is a laboratory method and preferred for its simplicity, convenience and accuracy. The third method is based on the cavity resonance. In this method sample is put inside the cavity and the resulting change in resonant frequency is used to estimate dielectric properties of the samples.

## Objectives of the proposed research

- To study temperature dependence of dielectric constant and dielectric loss ($\varepsilon'$ and $\varepsilon''$) of paracetamol and its two derivatives **[**N-(4-hydroxy-3-methylphenyl) ethanamide and N-(3,5-dimethyl-4-hydroxyphenyl) ethanamide**]** in dilute solutions at fixed frequencies using X-band and C-band microwave benches.

- To study frequency dependence of dielectric constant and dielectric loss ($\varepsilon'$ and $\varepsilon''$) of above mentioned polar aromatic compounds in dilute solutions in the frequency range 1-50 GHZ using Vector Network Analyser.

- To study dielectric constant and dielectric loss ($\varepsilon'$ and $\varepsilon''$) of binary mixtures at different frequencies and temperatures.

- To study dielectric constant and dielectric loss ($\varepsilon'$ and $\varepsilon''$) of ternary mixture of above mentioned compounds at different frequencies.

- To measure static and optical permittivity ($\varepsilon_0$ and $\varepsilon_\infty$) of paracetamol and its binary and ternary mixtures in dilute solutions.

- To calculate electric dipole moment of the samples by using dielectric parameters.

- To estimate thermodynamic parameters for both dielectric relaxation as well as viscous flow processes.

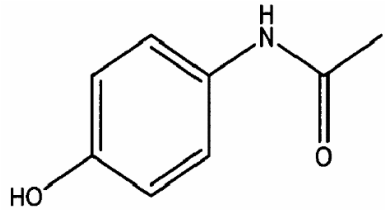
- To estimate the concentration of the chemicals under observation for which the absorption for the dielectric loss is maximum both in pure form and their binary and ternary mixtures.

**Materials:**

The proposed materials are paracetamol and its two derivatives:

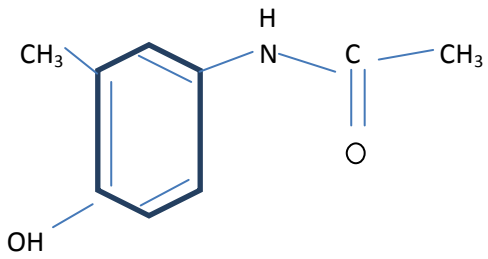
**Paracetamol:**

Paracetamol is one of the most common drugs used (Makin et al.,1994 ) in the world, and is manufactured in huge quantities (Miller et al., 1976) Paracetamol is used to treat headache, muscle aches, arthritis, backache, toothaches, colds and fevers. Its chemical formula is $CH_3CONHC_6H_4OH$. Its molecular weight is 151.17[g/mol]. (Penna et al., 1991 ) It is available in the form of white crystalline powder. It is soluble in water. Its IUPAC name is N-(4-hydroxyphenyl) and represented by the symbol

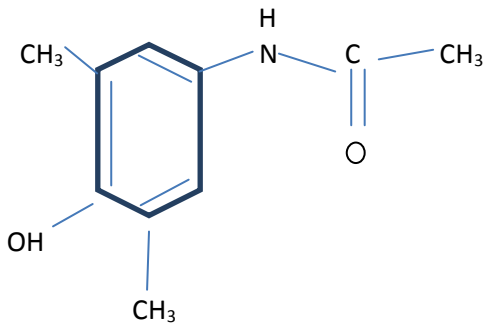


## Derivatives of paracetamol:

**(i) N-(4-hydroxy-3-methylphenyl)ethanamide**




**(ii) N-(3,5-dimethyl-4-hydroxyphenyl)ethanamide**



## Some properties of the derivatives of paracetamol

These are an antipyretic, non-steroidal anti-inflammatory drugs. They are soluble in organic solvents, such as methanol and ethanol but slightly soluble in water and ether. These derivatives are nonprescription analgesic and antipyretic drugs similar to aspirin. These derivatives stable to temperature, light, and moisture. They are also used as intermediate for pharmaceuticals (as a precursor in penicillin) and azo dyes, and as stabilizer for hydrogen peroxide and photographic chemicals. These derivatives are used in the treatment of arthritic and rheumatic conditions involving musculoskeletal pain and in other painful disorders, such as headache, dysmenorrhoea, myalgia and neuralgia.

## Methodology

### Vector Network Analyser Method:

The measurement of the reflection and/or transmission through a material along with the knowledge of its physical dimensions provides the necessary information to characterize the permittivity and permeability of the material. A vector network analyzer consists of a signal source, a receiver and a display (Agilent, 2006). The source launches a signal at a single frequency to the material under test. The receiver is tuned to that frequency to detect the reflected and transmitted signals from the material. The measured response produces the magnitude and phase data at that frequency. The source is then stepped to the next frequency and the measurement is repeated to display the reflection and transmission measurement response as a function of frequency.

Simple components and connecting wires that perform well at low frequencies behave differently at high frequencies. At microwave frequencies wavelength become small compared to the physical dimensions of the devices such that two closely spaced points can have a significant phase difference. Low frequency lumped-circuit element techniques must therefore be replaced by transmission line theory to analyze the behavior of devices at higher frequencies. Additional high frequency effects, such as radiation loss, dielectric loss and capacitive coupling make microwave circuits more complex and expensive. It is time consuming and costly to try to design a perfect microwave network analyzer.

It is also used to eliminate the systematic (stable and repeatable) measurement errors caused by the imperfections of the system. Random errors due to noise, drift, or the environmental changes (such as, change in temperature, humidity and pressure) cannot be removed by a measurement calibration. This makes a microwave measurement susceptible to errors from small changes in the measurement system. These errors can be minimized by adopting good measurement practices, such as visually inspecting all connectors for dirt or damage and by minimizing any physical movement of the test port cables after the calibration.

Impedance analyzers and LCR meters are used to measure the material properties at lower frequencies. The material is stimulated with an AC source and the actual voltage across the material is monitored. Material test parameters are derived by knowing the dimensions of the material and by measuring its capacitance and dissipation factor.

## Different Components of a Vector Network Analyser

### i) Fixtures

Before the dielectric properties of a material can be measured with network analyzer, impedance analyzer, or LCR meter, a measurement fixture (or sample holder) is required to apply the electromagnetic fields in a predictable way and to allow connection to the measuring instrument.

The type of fixture required depends on the chosen measurement technique and the physical properties of the material (solid, liquid, powder, gas).

**ii) Software**

The measured data from the instrument is not always presented in the most convenient terminology or format. In this case, software is required to convert the measured data to permittivity or permeability. Software may also be required to model any interaction between the fixture and MUT to allow the extraction of the bulk material properties.

**iii) Coaxial probe**

The open-ended coaxial probe is a small section of a transmission line with the other end connected to a probe. The dielectric properties of the material are measured by immersing the probe into a liquid or touching it to the flat face of a solid (or powder) material. The fields at the probe end "fringe" into the material and change as they come into contact with the MUT (fixture). A typical measurement system using a coaxial probe method consists of a network or impedance analyzer, a coaxial probe and software. Both the software and the probe are included in the dielectric probe kit. An external computer is needed in many cases to control the network analyzer through GP-IB. The USB to GP-IB interface provides a convenient and flexible way to realize this connection.

There are three types of probes available

1. High temperature probe
2. Slim form probe and
3. Performance probe

The high temperature probe features a hermetic glass-to-metal seal, which makes it resistant to corrosive or abrasive chemicals. The probe withstands a wide range (–40 to +200°C) of temperature which allows to take measurements for variation of the dielectric properties of materials over a wide range of frequency and temperature. The probe with large flange also

allows to take measurements of dielectric properties of flat surfaced solid materials, in addition to liquids and semi-solids.

The slim form probe features a slim design, which allows it to fit easily in fermentation tanks, chemical reaction chambers, or other equipment with small apertures. The slim design also allows it to be used with smaller sample sizes. This probe is best used for liquids and soft semi-solids. For cast able solids, the probe is economical enough to be casted into the material and left in place. Because of the consumable nature of this design, these probes are offered in sets of three.

The performance probe combines rugged, high temperature and frequency performance in a slim design, perfect for the most demanding applications. The probe can be autoclaved, so it is perfect for applications in the food, medical, and chemical industries where sterilization is a must.

Before measuring, calibration at the tip of the probe must be performed. A three-term calibration provided necessary correction for the directivity, tracking and source match errors that can be present in a reflection measurement. In order to correct for these three error terms, three well-known standards are used. The difference between the predicted and actual values is used to remove the systematic (repeatable) errors from the measurement. The three known standards usually taken are air, a short circuit and distillated and de-ionized water. Even after calibrating the probe, there are additional sources of error that can affect the accuracy of a measurement. There are three main sources of errors:

- Cable stability
- Air Gaps
- Sample thickness

It is important to allow enough time for the cable (that connects the probe to the network analyzer) to stabilize before making a measurement and to be sure that the cable is not flexed between calibration and measurement. The automated Electronic Calibration Refresh feature

recalibrates the system automatically, in seconds, just before each measurement is made. This virtually eliminates cable instability and system drift errors.
For solid materials, an air gap between the probe and sample can be a significant source of error unless the sample face is machined to be at least as flat as the probe face. For liquid samples air bubbles on the tip of the probe can act in the same way as an air gap on a solid sample.

The sample must also be thick enough to appear "infinite" to the probe. There is a simple equation to calculate the approximate minimum thickness of the sample required for the high temperature probe sample and the suggested thickness provides good material for the slim probe sample. A simple practical approach is to put a short behind the sample and check to see if it affects the measurement results.

**Dipole Meter:**

Dipole Meter is an adaptable instrument that is used for measuring the dielectric constant or static permittivity of non-polar liquids, Mittal Enterprises (2008). In this equipment a particular circuit has been developed for audio oscillator that produces stabilized oscillation. In this experiment dielectric cell is standardized using reference liquid having known dielectric constant by immersing the dielectric cell assembly in to the reference liquid. Then experimental liquid whose dielectric constant has to be determined is taken and the assembly is immersed into the experimental liquid, and the resulting change in the oscillation frequency is noted. From the resulting shift in frequency, change in the capacitance of cell immersed in unknown liquid is calculated ($C_x$). Dielectric Constant of unknown liquid is calculated by using the relation:

$$\varepsilon = 1 + \frac{C_0 - C_X}{C_0 - C_{SR}} (\varepsilon_{SR} - 1)$$

where

$C_0$ = Capacitance of Air,

$C_{ST}$ = Capacitance of standard liquid,

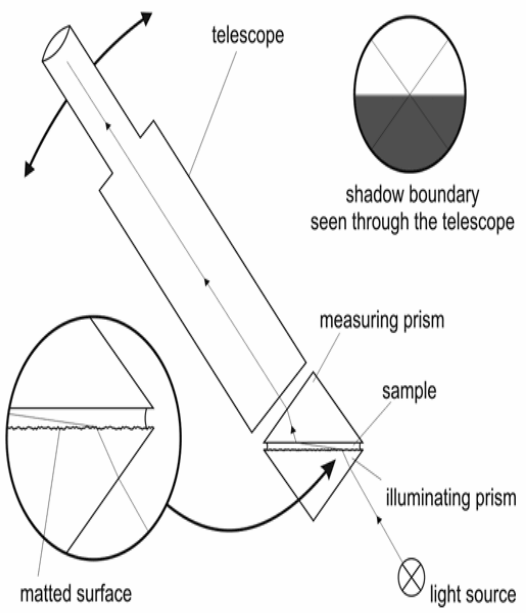
$C_X$ = Capacitance of test liquid and

$\varepsilon_{ST}$ = dielectric constant of standard liquid

**Abbe's Refractometer :**

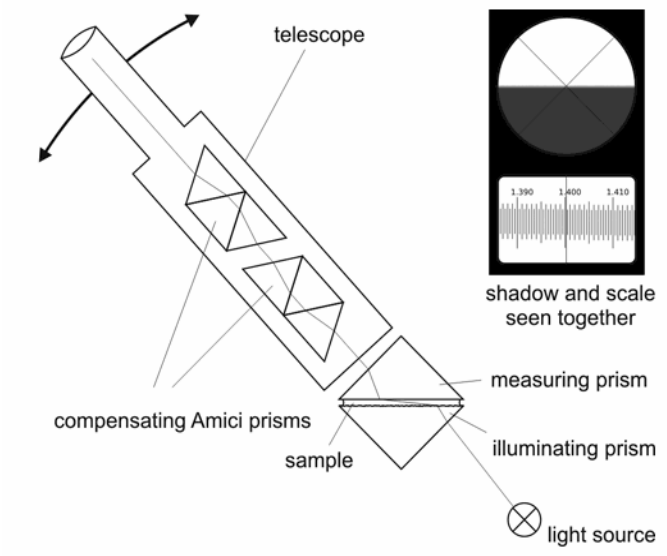
Abbe's refractometer's is used to find refractive index and hence dielectric constant at an optical frequencies of the liquid samples, to study the variation of refractive index at an optical frequency with temperature of the liquid sample and wavelength of the light source. It can also be used to determine the polarisability of the given liquid samples at a given temperature.

Abbe's refractometers working principle is based on critical angle. Sample is put between two prisms, called measuring and illuminating prisms. Light enters sample from the illuminating prism, gets refracted at critical angle at the bottom surface of measuring prism, and then the telescope is used to measure position of the border between bright and light areas. The telescope reverts the image, so the dark area is at the bottom, even if we expect it to be in the upper part of the field of view. Knowing the angle and refractive index of the measuring prism it is not difficult to calculate refractive index of the sample. Surface of the illuminating prism is matted, so that the light enters the sample at all possible angles, including those almost parallel to the surface.




**Abbé type crtitical angle refractometer**

While the image given above explains the basic principle, it is not yet a complete design of the Abbe's refractometer. Refractive index of a substance is a function of a wavelength. If the light source is not monochromatic (and in simple devices it rarely is) light gets dispersed and shadow boundary is not well defined, instead of seeing sharp edge between white and black, we see a blurred blue or red border. In most cases that means measurements are either very inaccurate or even impossible. To prevent dispersion Abbe's added two compensating Amici prisms into his design. Not only telescope position can be changed to measure the angle, also position of Amici prisms can be adjusted, to correct for the dispersion. In effect the edge of the shadow is well defined and easy to locate.




**( <u>Abbe's refractometer</u> )**

Original design made use of two telescopes - one was used to locate shadow boundary, the other to read the result. Modern devices combine both views so that we can read the result immediately, without a need for checking the other view. Some specialized devices may have double scale - one can be used for reading refractive index, the other (situated below or above, and visible at the same time) can be scaled in degrees Brix or concentration of some substance. Abbe's refractometer can be used to measure both refractive index of liquids and solids. In both the cases refractive index of the substance must be lower than the refractive index of the glass used to make the measuring prism.

To use the refractometer we simply put the sample between illuminating and measuring prisms, use rotating knob to place the shadow boundary on the telescope cross hairs, and read the refractive index from the scale. Liquid samples must be non corrosive, not to damage surface of the prisms. Abbe's refractometers can give an accuracy of about one to two units in the fourth decimal place.

It is worth noting here, that, as refractive index changes with temperature, for a correct result of refractive index measurement we have to either use thermo stated sample, or - after measuring the refractive index-measure temperature and read correction from tables. Most laboratory models of Abbe's refractometers can be readily attached to the source of constant temperature water bath.

## Measurement of $\varepsilon'$ and $\varepsilon''$:

The values of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) at different frequencies will be determined by using a Vector Network Analyzer. The values of dielectric permittivity at low frequencies ($\varepsilon_0$) and at optical frequencies ($\varepsilon_\infty$) will be determined by using a dipole meter and Abbe's refractometer respectively (Jain et al., 2012) All the measurements will be performed at different temperatures using a constant temperature circulating water bath fitted with a thermostat having temperature stability of the order of ± 0.1°C.

For dilute solutions in non-polar solvents $\varepsilon'$, $\varepsilon''$, $\varepsilon_0$ and $\varepsilon_\infty$ can be expressed as linear functions of concentrations (Franklin et al, 1950; Higasi, 1966) in the following manner:

$$\varepsilon' = \varepsilon_1' + a' W_2 \quad (1)$$

$$\varepsilon'' = a'' W_2 \quad (2)$$

$$\varepsilon_0 = \varepsilon_{10} + a_0 W_2 \quad (3)$$

$$\varepsilon_\infty = \varepsilon_{1\infty} + a_\infty W_2 \quad (4)$$

Here subscript 1 refers to the pure solvent, 2 to the solute, while 0 refers to the static or low frequency case and ∞ refers to the infinite or optical frequency case, $W_2$ is taken as the weight fraction of the solute. a', a'', $a_0$ and $a_\infty$ are the slopes of above mentioned linear equations. The values of the relaxation times $\tau_0$, $\tau_1$, and $\tau_2$ are calculated by using the method given by Higasi et al (Higasi et al, 1971). The relaxation time for overall molecular rotation ($\tau_1$) is defined by

$$\tau_1 = \frac{1}{\omega} \left\{ \frac{a''}{a' - a\alpha_\infty} \right\} \quad (5)$$

Whereas the relaxation time for intermolecular rotations ($\tau_2$) is given by

$$\tau_2 = \frac{1}{\omega}\left\{\frac{a_0 - a'}{a''}\right\} \qquad (6)$$

Here ω is the angular frequency corresponding to the microwave frequency at which the experiment is performed. The most probable relaxation time ($\tau_0$) is then obtained by employing the following relation:

$$\tau_0 = \frac{1}{\omega}\frac{\left[\left(A\right]^2 + B^2\right)^{\frac{1}{2(1-(}}}{\left(C^2\right)} \qquad (7)$$

where

$$1-\ \alpha = \frac{2}{\pi}\tan^{-1}\frac{A}{B} \qquad (8)$$

and

$A = a''(a_0 - a_\infty)$

$B = (a_0 - a')(a' - a_\infty) - (a'')^2$

$C = (a' - a_\infty)^2 (a'')^2$

The value of the dipole moment (μ) of the solute molecules is calculated by using Higasi's method. According to this method the value of dipole moment is given by

$$\mu = \left[(27kTM_{12})/(4\pi N d_{11}\left[(\epsilon_{101} + 2)\right]^{\uparrow}2))\right]^{\uparrow}((a_{10} - a_{1\infty})) \qquad (9)$$

Where $M_2$ is the molecular weight of solute, $d_1$ is the density of solvent, k is the Boltzmann constant, N is the Avogadro's number and T is the temperature in Kelvin at which the experiment

is performed. Thus knowing the value of $a_0$ and $a_\infty$, $\mu$ can be obtained from equation (9) at different temperatures.

**Dielectric Relaxation Process**

The temperature dependence of relaxation time has been utilized to obtain the value of molar free energy of activation $\Delta F_\varepsilon$, molar enthalpy $\Delta H_\varepsilon$ and molar entropy $\Delta S_\varepsilon$. From the theory of relaxation time as rate process developed by Eyring, the relaxation time is given by

$$\tau = \frac{A}{T} \cdot \exp\left(\frac{\Delta F_\varepsilon}{RT}\right) \qquad (10)$$

In which

$$\Delta F_\varepsilon = \Delta H_\varepsilon - T\Delta S_\varepsilon \qquad (11)$$

Where A= h/k and the other symbols have their meaning.

Now following three cases may arises:

(1) Taking logarithms of both sides of equation (10), we get

$$\Delta F_\varepsilon = RT \ln\left(\frac{kT\tau}{h}\right) \qquad (12)$$

After knowing the values of $\tau$ and T, the value of $\Delta F_\varepsilon$ can be calculated.

(2) From equations (10) and (11) we may write

$$\ln(\tau T) = \ln\left(\frac{h}{k}\right) + \frac{1}{RT}\left(\Delta H_\varepsilon - T\Delta S_\varepsilon\right) \qquad (13)$$

When ln(τT) is plotted against 1/T, a straight line is obtained, whose slope on multiplication with R gives the value of $\Delta H_\varepsilon$ .

(3) Knowing $\Delta F_\varepsilon$ and $\Delta H_\varepsilon$, $\Delta S_\varepsilon$ can be calculated from the relation

$$\Delta F_\varepsilon = \Delta H_\varepsilon - T\Delta S_\varepsilon \qquad (14)$$

### 3.11.2 Viscous Flow Process

Eyring's equation for the viscous flow rate process is given by

$$\eta = B \exp\left(\frac{\Delta F_\eta}{RT}\right) \qquad (15)$$

Where $$\Delta F_\eta = \Delta H_\eta - T\Delta S_\eta \qquad (16)$$

Where B = hN/V and 'V' is the molar volume which is equal to M/d; 'M' is the molecular weight, 'd' is the density and 'η' is the viscosity of the non-polar solvent at temperature T K.

(1). Taking logarithm of equation (15), we get

$$\Delta F_\eta = RT \ln\left(\frac{V\eta}{hN}\right) \qquad (17)$$

Knowing the values of η, V and T, $\Delta F_\eta$ can be calculated.

(2). From equations (15) and (16), we may write

$$\ln \eta = \ln\left(\frac{hN}{V}\right) + \frac{1}{RT}\left(\Delta H_\eta - T\Delta S_\eta\right) \qquad (18)$$

Plot of ln η against 1/T gives a straight line whose slope $\Delta H_\eta/R$, when multiplied with gas constant 'R' gives the value of $\Delta H_\eta$.

(3). Knowing $\Delta F_\eta$ and $\Delta H_\eta$ ,$\Delta S_\eta$ can be calculated from the equation

$$\Delta F_\eta = \Delta H_\eta - T\Delta S_\eta$$

## Interdisciplinary Relevance

Dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$) and dielectric relaxation in the binary mixtures of edible oils provide a method for quality check to the purity of sample at microwave frequencies, (Agarwal et al., 2005) The values of dielectric parameters of several ionic liquids (ILs) suggest that they might be used as electrolyte in batteries, at 2.45 GHz and at different temperatures. The dielectric characteristics also give information about the structure of the ionic liquids.

The dielectric parameters can also be affected by the dielectric properties of liquid crystal that belong to one homologous series ( Tripathi et al., 2013 ) The most dominating factors which influence the dielectric parameters are bridging group and polar sites. The microwave measurements and the dielectric properties of materials. are finding increasing application as new electro-technology is adapted for use in the agriculture and food processing industries (Venkatesh et al., 2005) These dielectric properties are an intermediatary vehicle for

understanding, explaining, and empirically relating certain physico-chemical properties of the test material. They also explore the existing knowledge of dielectric properties (complex permittivity), their role and importance in the agri-food sector and the concept of various measurement methodologies and their development.

For the study of polar oleic acid in the liquid phase Francisco Ferreira de Sousa (2010) used the static dielectric permittivity as a function of temperature. It was also observed by Bashi et al., (2006) that the dielectric properties of vegetable oils are renewable and environmentally friendly. They are also compatible for use as insulating transformers without any risk. This study shows that the palm oil has a very good potential to be used as a dielectric fluid, so the development and usage of dielectric fluid from palm oil base could ensure compliance to environmental and safety laws.

The cut and polished grown single crystal of 4-Methoxyaniline was used for dielectric studies because the dielectric characteristics of the material are important for the study of lattice dynamics in the crystal (Sagadevan et al., 2014). Dielectric measurements indicate that the dielectric constant and dielectric loss of the 4-Methoxyaniline single crystal decreases significantly with increasing frequency to make the crystal a more interesting material in the microelectronics industry.

## Plan of Work :

**First six month**

- Literature survey and learning about the details of material and methods.

**Next Six month**

- Study of dielectric properties of polar liquids in dilute solutions.
- Study the effect of temperature and frequency variation.
- Write research papers and get them published.

**Next Six month**

- Study of the dielectric parameters for binary samples and temperature and frequency variation for different concentration.
- Write research papers and get them published.

**Next Six month**

- Study of the dielectric parameters for ternary mixture and temperature and frequency variation for different concentration.
- Write research papers and get them published.
- Compilation of research work.
- Write the thesis.

## Expected outcomes:-

- These studies will provide information about the variation of dielectric parameters of paracetamol with frequency and temperature.
- The concentration of the sample will be calculated for the maximum absorption.
- Dielectric behavior of the derivatives of paracetamol shall be studied.

- Any structural changes in the composition of the sample will be investigated.

- The behavior of chemicals can be predicated, basically when two or more drugs are administered simultaneously.

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